

METHYLTIN CHLORIDES

5526

Formula: Table 1

MW: Table 1

CAS: Table 1

RTECS: Table 1

METHOD: 5526, Issue 1

EVALUATION: FULL

Issue 1: web 1 Jan 2002

OSHA : See Table 1

NIOSH: See Table 1

ACGIH: See Table 1

PROPERTIES: See Table 1

SYNONYMS: Methyltin Trichloride: Trichloromethylstannane, Monomethyltin trichloride
Dimethyltin Dichloride: Dichlorodimethylstannane, Dichlorodimethyltin
Trimethyltin Chloride: Chlorotrimethylstannane, Chlorotrimethyltin, Trimethylstannyl chloride

SAMPLING		MEASUREMENT	
SAMPLER:	FILTER + SORBENT TUBE (OVS Tube: 13-mm glass fiber filter; XAD-2, 270/140 mg)	TECHNIQUE:	GAS CHROMATOGRAPHY, FPD (tin-specific filter)
FLOW RATE:	0.25 to 1 L/min	ANALYTE:	Sodium tetraethylborate derivatives of the analytes
VOL -MIN:	15L	DESORPTION:	2 mL 1% Acetic Acid in Acetonitrile
-MAX:	75L	INJECTION VOLUME:	1 µL
SHIPMENT:	Ship assembled sampler cold	TEMPERATURE-INJECTION:	cool-on-column
SAMPLE STABILITY:	14 days @ 4 °C	-DETECTOR:	250 °C
FIELD BLANKS:	2 to 10 field blanks per set	-COLUMN:	50 °C (3min), 12°C/min to 200°C (1min)
ACCURACY		CARRIER GAS:	He, 6 mL/min
RANGE STUDIED:	Table 2	COLUMN:	capillary, fused silica, 30m x 0.53mm ID, 1.5-µm film, 5% phenyl, 95% methyl silicone, DB-5 or equivalent.
BIAS:	Table 2	CALIBRATION:	analytes in hexane
OVERALL PRECISION (\hat{S}_{rt}):	Table 2	RANGE:	0.01 to 15 µg/sample (as tin) [1]
ACCURACY:	Table 2	ESTIMATED LOD:	0.01 µg [1]
		PRECISION (\hat{S}_s):	0.065 [1]

APPLICABILITY: This method was developed for air monitoring of methyltin chlorides.[1]

INTERFERENCES: None were identified.

OTHER METHODS: NMAM 5504 is another method for the measurement of Organotin compounds using a filter with a sorbent tube for collection and HPLC/AA for analysis.[3]

REAGENTS:

1. Acetic Acid, 99+%.
2. Acetonitrile, HPLC grade.
3. Diethyl Ether, 99+%.
4. Hexane, HPLC grade.
5. Methyltin Trichloride, 97%.
6. Dimethyltin Dichloride, 97%.
7. Trimethyltin Chloride.
8. 1% acetic acid in acetone solution, (v/v).
9. Sodium Tetraethyl borate.*
NOTE: Purity of sodium tetraethyl borate is critical. It should appear as a fine white powder. Clumping or yellowing indicates that the compound must be replaced.
10. Sodium Acetate - Acetic Acid Buffer, pH 4.0 ± 0.2 . Commercially available from Fisher Scientific.
11. Derivatizing Solution: Prepare a solution containing 1% (w/v) of sodium tetraethylborate in diethyl ether.* Prepare the solution fresh daily, preferably immediately before use.
12. Calibration Stock Solution: Prepare a stock calibration solution by accurately weighing (to ± 0.1 mg) about 0.1 g each of methyltin trichloride, dimethyltin dichloride and trimethyltin chloride into a 50 ml volumetric flask. Dilute to volume with 1% acetic acid in acetonitrile. The stock solution contains about 1000 $\mu\text{g/ml}$ (as tin) of each component. Stored in a freezer, this solution remains stable for several weeks.

EQUIPMENT:

1. Sampler: OSHA Versatile Sampler (OVS tube), 13-mm OD inlet, 6-mm OD outlet. Front section contains 270 mg 20/60 mesh XAD-2 sorbent held in place by an 11-mm diameter glass fiber filter and Teflon® ring, separated from the back section of 140 mg XAD-2 sorbent by a short plug of polyurethane foam. The back section is held in place with a plug of polyurethane foam. The tube is available commercially from SKC, Inc. (cat. #226-30-16) and Supelco, Inc. (cat. #ORBO-49P).
2. Personal sampling pump: 0.1 to 1 L/min with flexible and inert connecting tubing.
3. Gas chromatograph equipped with a cool on-column injection port, automated injector, DB-5 capillary column, flame-photometric detector (FPD) with a tin-specific filter (610 nm), and data collection system or equivalent (page 5526-1).
4. Balance capable of weighing to ± 0.1 mg.
5. Mechanical shaker.
6. Vials, 10mL, with PTFE-lined screwcaps.
7. Transfer pipettes or eyedroppers.
8. GC autosampler vials with PTFE-lined caps.
9. 5, 10 and 50 mL volumetric flasks.
10. Pipettes capable of accurately delivering 10 μL and 1.0 and 2.0 mL.
11. Refrigerant packs for shipping.

* See SPECIAL PRECAUTIONS

SPECIAL PRECAUTIONS: Sodium Tetraethylborate is sensitive to air and moisture! This chemical should be stored and handled under a nitrogen atmosphere. Acetonitrile, diethyl ether, and hexane are all flammable. Wear appropriate protective clothing and work with these compounds in a well ventilated hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Uncap the sorbent tube immediately before sampling and connect to a personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.25 L/min for full shift sampling and 1 L/min for 15 minutes samples (STEL) for a maximum of 75 L.
4. Cap the samplers. Pack securely for shipment with cold refrigerant packs.
NOTE: After receipt at the laboratory, samples should be stored at 4°C and analyze within 14 days of collection.

SAMPLE PREPARATION:

5. Remove the retaining ring from the sorbent tube and discard. Transfer the glass fiber filter and the main resin bed to a 10-mL sample vial.
6. Remove and discard the foam plug that separates the two resin sections in the sorbent tube. Transfer the backup resin bed to a second 10-mL sample vial.
7. Into each vial, add 2 ml of 1% acetic acid in acetonitrile to desorb the methyltin chlorides. Put the vials on a mechanical shaker for 30 minutes.
8. Into each vial, add 2 ml of pH 4 buffer and 1 ml of derivatizing solution. Place the vials on the mechanical shaker for 15 minutes.
9. Extract the solution with three 1 ml portions of hexane. Combine the hexane fractions in a 5 ml volumetric flask and dilute to volume with hexane.

CALIBRATION AND QUALITY CONTROL:

10. Calibrate daily with at least six working standards over the range of interest.
 - a. Accurately pipette 10 μ l of the calibration stock solution into a vial that contains 2ml of 1 % acetic acid in acetonitrile. Treat as a sample following steps 7 through 9. This is the highest concentration standard, containing about 2 μ g/ml (as tin) of each methyltin chloride.
 - b. Serially dilute this standard solution with hexane to produce solutions over the range of 0.2 to 0.02 μ g/ml (as tin) of each methyltin chloride.
 - c. Transfer to gc autosampler vials with PTFE-lined caps.
 - d. Analyze together with samples and blanks (steps 12 through 14).
 - e. Prepare calibration graph (peak areas vs. μ g tin for each methyltin chloride).
11. Determine desorption efficiency (DE) at least once for each lot of OVS tubes used for sampling in the calibration range (step 10). Prepare three samplers at each of six levels plus three media blanks.
 - a. Transfer the front sorbent section of the OVS sampler to a 4mL vial.
 - b. Inject a known volume of calibration stock solution, or a serial dilution of, directly onto the front sorbent bed of each OVS tube.
 - c. Cap vial and allow spiked sorbent bed to stand overnight.
 - d. Desorb (steps 7 through 9) and analyze together with standards and blanks (steps 13 through 15).
 - e. Prepare a graph of DE vs. μ g for each methyltin chloride recovered.
12. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graphs are in control.

MEASUREMENT:

13. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 5526-1.
14. Inject a 1- μ L sample aliquot manually using solvent flush technique or with an autosampler.
NOTE: If peak area is above the linear range of the working standards, dilute with hexane, reanalyze, and apply the appropriate dilution factor in the calculations.
15. Measure the areas of the peaks of the methyltin chlorides. A sample chromatogram is shown in Figure 1.

CALCULATIONS:

16. Determine the mass, μ g (corrected for DE), for each methyltin chloride found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
17. Calculate concentration, C, of each methyltin chloride in the air volume sampled, V (L):
NOTE: μ g/L \equiv mg/m³

$$C = \frac{(W_f + W_b - B_f - B_b)}{V}, \text{mg} / \text{m}^3$$

EVALUATION OF METHOD:

This method, developed to collect air samples and analyze the methyltin chlorides, was adapted from existing methodology for measuring organotin compounds in air.[3,4] Reference 1 details the validation of this method for sampling and quantifying of trimethyltin chloride, dimethyltin dichloride and methyltin trichloride in air. The validated method was needed to provide air monitoring capabilities during methyltin chloride and stabilizer production. Table 2 lists the results of the validation experiments which followed the guidelines established by NIOSH [2]. However, fewer replicates and concentration levels were used than recommended. This method met the NIOSH criteria for accuracy, bias and sample stability. The recommended sampling conditions are 250 ml/min for 5.5 hours maximum for time-weighted average (TWA) sampling and 1000 ml/min for 20 minutes maximum for short-term exposure limit (STEL) sampling.

REFERENCES:

- [1] Yoder RE [2000]. Validation of a Method for the Collection and Quantification of Methyltin Chlorides in the Air. Philadelphia, PA: Atofina Chemicals. Unpublished.
- [2] NIOSH [1995]., Guidelines for Air Sampling and Analytical Method Development. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 95-117.
- [3] NIOSH [1994]. Organotin Compounds (as Sn): Method 5504. In: Eller PM, Cassinelli ME, eds. NIOSH Manual of Analytical Methods, 4th Ed. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 94-113.
- [4] Shangwei H [1997]. Development of a Method for the Sampling and Analysis of Dimethyltin Dichloride and Trimethyltin Chloride [Dissertation]. New Orleans, LA: Tulane University, Department of Environmental Sciences, School of Public Health and Tropical Medicine.

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TABLE 1. GENERAL INFORMATION

Analyte	Formula	Mol. Wt.	CAS#	RTECS#	Properties	OSHA PEL ^a (mg/m ³)	NIOSH REL ^b (mg/m ³)	ACGIH TLV ^c (mg/m ³)
Methyltin trichloride	CH ₃ Cl ₃ Sn	240.04	993-16-8	WH858550	Colorless Crystals MP 48-51°C BP 171°C	0.1	0.1	0.1 0.2 STEL (skin)
Dimethyltin dichloride	C ₂ H ₆ Cl ₂ Sn	219.67	753-73-1	WH7245000	Colorless Crystals MP 103-105°C BP 188-190°C	0.1	0.1	0.1 0.2 STEL (skin)
Trimethyltin chloride	C ₃ H ₉ ClSn	199.25	1066-45-1	WH685000	Colorless Crystals MP 37-39°C BP 154 °C	0.1	0.1	0.1 0.2 STEL (skin)

^a - OSHA PEL is measured as the amount of Tin (Sn) for organotin compounds in air

^b - NIOSH REL is measured as the amount of Tin (Sn) for organotin compounds in air

^c - ACGIH TLV is measured as the amount of Tin (Sn) for organotin compounds in air

TABLE 2. METHOD EVALUATION [1]

	Range Studied	Bias (%)	Precision (S_{rT}) (%)	Accuracy (%)
Trimethyltin chloride	0.46 - 9.29 $\mu\text{g}/\text{sample}$ (tin)	0.3	5.2	11
Dimethyltin dichloride	0.42 - 9.17 $\mu\text{g}/\text{sample}$ (tin)	-2.5	5.8	12
Methyltin chloride	0.07 - 10.48 $\mu\text{g}/\text{sample}$ (tin)	-5.2	7.6	16

